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LIGHT SENSITIVE MATERIALS CONTAINING LIGHT SENSITIVE DIAZO COMPOUNDS

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The present invention relates to light sensitive materials containing light sensitive diazo compounds.

It is known that amino diazo compounds alone or in mixture with azo components are suitable for the production of light sensitive layers. The choice of diazo compounds for the so-called semi-wet process (a process wherein the base or support only carries the diazo compound and the image is produced after exposure by the application of a solution of an azo component) is however small if the quality of the layers and the copies is to be such as to meet far reaching requirements. The layers produced must, for practical purposes, not only be stable for weeks in the undeveloped state, but it is also requisite that the copies should exhibit sharp outlines and a clean ground. In addition to this the light sensitiveness of the layers must be high and the images must be capable to be developed easily with only a small amount of alkali, in order that thet sizing of the paper should not be attacked. Furthermore, it is necessary that as far as possible when the finished copies are exposed to light no yellowing or bronzing of the ground should take place. There are only a few diazo compounds which fulfill to a sufficient extent these practical requirements.

The applicants have found that amongst the secondary amino diazo compounds, of which hitherto only diazo diphenylamine has proved practically applicable, for the production of light sensitive layers the diazo compounds of benzyl-amino-aryl-amines which contain at least one halogen atom in the benzyl residue, are particularly appropriate. These compounds correspond with the following general formula

$$NH_2—R.NH—CH_2—R'$$

wherein R is a substituted or non-substituted aromatic nucleus preferably a benzene nucleus and R' is a halogenized benzene nucleus which may contain further substituents.

In connection herewith it was found that diazo compounds which contain at least one halogen atom in the ortho position to the CH_2 group of the benzyl residue are particularly useful. 1-diazo-2'.4'-dichlorbenzyl-4-aniline and particularly also 1-diazo-2'.6'-dichlorbenzyl-4-aniline have proved very advantageous. The compounds may also contain in the aniline and benzyl residue further substituents such as alkyl, halogen, cyan and alkoxy or aryloxy groups, whereby small variations in the colour of the copies can be obtained. The diazo compounds used may be employed in the customary manner, for example, by coacting a support with the solution or by impregnating a support with the solution. Naturally it is also possible to use the diazo compound in question together with an azo component. The light sensitive materials thus obtained are, after exposure, developed by means of gaseous ammonia. In some cases it may be suitable to add to the light sensitive solution or layer containing as light sensitive matter the diazo compounds mentioned above, a small quantity of another light sensitive more coloured diazo compound for colouring the layer more strongly whereby it is facilitated to distinguish the bleaching out of the layer during exposure. For this purpose there is suitable an addition of for instance 1-2 parts by weight of the sulphate of the diazotized p-amino-diphenyl-amine. It is also possible to add small quantities of another light sensitive, rapidly coupling diazo compound to the layer for varying the shades of the copies and for influencing the fastness to light of the dyestuffs formed in the copy. Diazotized amino-carbazol has proved to be suitable for this purpose.

It is true that besides diazo diphenylamine some secondary diazo amino compounds are known which contain a large residue, for instance the tetraline residue, but these compounds are excelled in quality by the new compounds according to the present invention. Furthermore it has already been proposed to employ diazo compounds which contain a benzylamino residue and if desired also contain further residues in the NH group. From these known products the new compounds according to the invention differ essentially inasmuch as they have a halogen substituent in the benzyl nucleus. It is just the halogen atoms in the externally located benzyl residue which produce the surprising result that the new compounds have considerably better properties for photographic printing purposes than the known compounds. For example they exhibit better stability, are easily obtainable with good yields and furthermore provide the possibility of obtaining with ease dark shades which, as is well known, are particularly desirable in diazo type work. Moreover the compounds used according to the invention offer the further advantage of possessing a greater degree of light sensitiveness and a very high speed of coupling. This latter property is of particular importance in practice, particularly for the so-called wet process, inasmuch as the necessary developing

solution only needs to be very slightly alkaline and in spite of this a rapid and complete coupling is obtained. In addition to this the destruction of the sizing of the paper is no longer to be feared.

The following examples illustrate the invention:

	Parts by weight
(1) Tartaric acid or citric acid or another organic acid	10
Boric acid	10
Aluminium sulphate	20
Thiourea	40
Zinc salt of 4-(dichlorbenzyl-2'-6')-amino-1-diazo-benzene	20

are dissolved in water to give 1000 parts by volume and are applied in the usual manner to a base, for example paper. After exposure under a positive or negative the image is developed, for example by applying by means of a roller an alkaline solution of a coupling component which may, for example, be of the following composition:

	Parts by weight
Soda	10
Trisodiumphosphate	20
Borax	20
Sodium chloride	80
Phloroglucine	3

dissolved in 1 litre of water. It will, of course, be understood that a mixture of several azo components may likewise be employed, and the usual additions for improving stability, moistening means and so forth may be added. By the use of the said developer deep black lines on a good white ground are obtained. The said diazo compounds exhibit a great advantage in particular in the copying of pencil drawings. In this case fine blue black shades are obtained whilst with most diazo compounds reddish shade copies are produced.

Instead of the 2'.6'-dichlorbenzyl compound a similar quantity of the 2'.4'-dichlor compound can be used. Similar tones are obtained in this case whilst the sensitiveness to light is also equally good. It is also possible to introduce into the benzene nucleus in which the diazo group is located other substituents. In this way for example by substitution in the 3-position by the —O.CH_3— or —O.C_2H_5— group a somewhat more strongly coloured diazo compound, the light sensitiveness of which is also somewhat higher and which yields brownish-black shades, is obtained and can also be used in the preceding example instead of the mentioned diazo compound.

The diazo compounds can be prepared in the usual way. For example diazotized sulphanilic acid may be coupled with 2.6-dichlorbenzylaniline obtained by the condensation of dichlorbenzylchloride with aniline, in a strong acetic acid solution so as to form an azo dyestuff. The dyestuff is then reduced by means of hydrosulphite and the resulting p-amino-dichlorbenzylaniline is diazotized in a strong hydrochloric acid solution. After the diazotization heat is applied until the resulting nitrosodiazo compound is decomposed and the normal diazo compound is obtained, which can be recognized by the fact that when this stage is reached the product does not couple with alkaline R-salt solution to form a red colouring matter but couples slowly to form a violet colouring matter. The diazo compound is thereupon separated preferably in the form of the zinc chloride double salt.

	Parts by weight
(2) Tartaric acid	15
Boric acid	10
Aluminium sulphate	20
Thiourea	45
Zinc chloride salt of the diazo compound of 1-amino-4-[trichlorbenbyl (2',4',6']-aminobenzene	18

are dissolved in 1000 parts by volume of water and are applied to paper. After development with a solution of approximately the following composition:

	Parts by weight
Soda	8
Trisodiumphosphate	15
Borax	8
Sodium acetate	60
Sodium chloride	40
Phloroglucine	3
Resorcin	1

dissolved in 1 litre of water, fine blue black copies are obtained. For avoiding a yellowing of the back ground of the diazo types in a beter degree it may be suitable to add 60 parts by weight of sodium thiosulphate or 50 parts by weight of thiourea to the developing solution described above.

(3) Instead of the diazo compound set forth in the preceding Example 2, 26 parts by weight of the zinc chloride salt of the diazo compound of 1-amino-4-[tetrachlorbenzyl] (2',3',4',6')]-aminobenzene are employed. The diazo compound which likewise couples rapidly gives copies of somewhat browner shades than those obtained according to Example 2.

(4) A solution of

	Parts by weight
Citric acid or oxalic acid	15
Boric acid	10
Ammonium sulphate	10
Aluminium sulphate	15
Thiourea	40
Zinc chloride salt of the diazo compound of 1-amino-3-phenoxy-4-[dichlorbenzyl-(2',6')]-aminobenzene, obtained by coupling 2,6-dichlorbenzl-o-aminodiphenylether with diazotized sulphanilic acid and subsequent reduction of the azo dyestuff	18

in 1 litre of water is applied to the base in the customary manner. The fairly strongly coloured diazo compound whilst possessing good light sensitiveness couples very rapidly and gives exceptionally beautiful shades from pencil drawings. Good results are obtained with very weak alkaline developing solutions without any danger of the lines running or spreading, which is an advantage as regards the subsequent ink stability of the prints. For example with a developer which contains

	Parts by weight
Borax	10
Sodium bicarbonate	30
Sodium chloride	70
Sodium acetate	50
Phloroglucine	4

dissolved in 1 litre of water, deep black or very beautiful dull blue gray shades are obtained just according to whether the copy has been made from an original executed in ink or pencil. If somewhat more alkaline developers are employed,

as for example the developer set forth in Example 1, browner shades are obtained.

(5) If the diazo compound set forth in Example 4 is replaced by 16 parts by weight of the sulphate of the diazo compound of 1-amino-2-chlor-4-[dichlorbenzyl - (2',6',)] - aminobenzene, prepared from 2.6 dichlorbenzylchloride and 4-amino-2-chloracetanilide with subsequent saponification of the acetyl group and diazotation of the resulting compound, then extremely rapidly coupling paper is likewise obtained. The development is carried out by means of a developer as specified in Example 4 or by means of a developer which is still more weakly alkaline and which may be of approximately the following constitution:

	Parts by weight
Sodium acetate	80
Sodium chloride	50
Phloroglucine	4
Resorcin	1

dissolved in 1 litre of water. Very beautiful blue black copies are obtained. Instead of sodium acetate other salts giving solutions of similar alkalinity may be employed, such as for example sodium adipinate, sodium malinate and so forth. By the further addition of small quantities of other weak alkalis, for example borax, sodium carbonate, or secondary sodium phosphate, it is possible to vary the shades to a certain extent.

(6) Instead of the diazo compounds set forth in the preceding Examples 1 and 4, 22 parts by weight of the sulphate of the diazo compound of 1-amino-2.5-dichlor-4-(dichlorbenzyl-2'.6') - amino-benzene are employed. This rapidly coupling diazo compound yields black to brownish-black shades when developed with the developing solutions described in Example 1 or 2.

(7) Instead of the diazo compound set forth in Example 4, 30 parts by weight of the cadmium-chloride-salt of the diazo compound of 1-amino-4-(trichlor-2'-4'-6'-cyan-3'-benzyl)-amino- benzene are employed. The paper thus obtained yields blue-black shades with a greenish tinge, when developed according to Example 4.

(8) Instead of the diazo compound set forth in Example 1, 22 parts by weight of the zinc chloride salt of the diazo compound of 1-amino-2-chlor-5-methoxy-4-(dichlor-2'-6'-benzyl)-amino-benzene are used for the preparation of the light sensitive layer. This diazo compound is more strongly coloured and couples more rapidly than the diazo compound mentioned in Example 1. It yields black shades with a reddish tinge.

(9) Instead of the diazo compound set forth in Example 1 there may be used the diazo compound of 1-amino-2-methyl-5-methoxy-4-(dichlor-2'-6'-benzyl)-amino-benzene. This compound is coloured feebly, couples more slowly and yields violet-tinged black shades with the developing solution described in Example 1.

(10) Instead of the diazo compound, set forth in Example 4, 22 parts by weight of the sulphate of the diazo compound of 1-amino-2-brom-4-(dichlor-2'-6'-benzyl)-amino-benzene are used in the light sensitive preparation disclosed in Example 1. The diazo compound couples extremely rapid and yields full dark blue-black shades when developed with the developing solution mentioned in Example 1.

(11) Instead of the diazo compound, set forth in Examples 1 and 4, corresponding quantities of the diazo compound of 1-amino-4-(brom-2'-chlor-6'-benzyl)-aminobenzene may be used. This compound yields brownish-black shades when developed with the solutions mentioned in Examples 1 and 4.

(12) The diazo compound used in Example 1 is replaced by 23 parts by weight of the zinc salt of the diazo compound of 1-amino-4-(dibrom-2'-6'-benzyl)-aminobenzene. This product yields bluish-black shades after development.

We claim:

1. Light sensitive materials containing as light sensitive matter a diazotized benzyl-amino-arylamine containing at least one halogen atom in the benzyl residue said arylamine being an arylamine of the benzene series.

2. Light sensitive materials containing as light sensitive matter a diazotized benzyl-amino-phenylamine containing at least one halogen atom in the benzyl residue.

3. Light sensitive materials containing as light sensitive matter a diazo compound obtained by diazotizing a product of the following general formula:

$$H_2N—R.NH.CH_2.R'$$

wherein R is a phenyl residue which is substituted by halogen, an alkyl residue, an alkoxy group or a phenoxy group, and R' a phenyl residue containing at least one chlorine or bromine atom.

4. Light sensitive materials containing as light sensitive matter the diazo compound of 1-amino-4-(dichlor-2'.6'-benzyl)-amino-benzene yielding, after exposure, a diazotype with deep black shades when developed with an alkaline solution of phloroglucine.

5. Light sensitive material containing as light sensitive matter the diazo compound of 1-amino-3 - phenoxy-4-(dichlor-2'6'-benzyl) - amino-benzene yielding, after exposure, a diazotype with deep black or dull blue-gray shades, when developed with an alkaline solution of phloroglucine.

6. Light sensitive material containing as light sensitive matter the diazo compound of 1-amino-2 - chlor-4-(dichlor-2'.6'-benzyl) - amino-benzene yielding, after exposure, a diazotype with blue-black shades, when developed with an alkaline solution of phloroglucine.

7. Light sensitive material containing as light sensitive matter a diazotized benzyl-amino-phenylamine containing at least one chlorine atom in the benzyl residue.

8. Light sensitive material containing as light sensitive matter a diazotized benzyl-amino-phenylamine containing at least one chlorine atom in the benzyl residue in the ortho-position to the CH_2-group.

9. Light sensitive material containing as light sensitive matter a diazotized benzyl-amino-arylamine containing at least one chlorine atom in the benzyl residue, said arylamine being an arylamine of the benzene series.

10. Light sensitive material containing as light sensitive matter a diazotized benzyl-amino- arylamine containing at least one chlorine atom in the benzyl residue in the ortho-position to the CH_2-group, said arylamine being an arylamine of the benzene series.

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